NOTES

Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie

Abstract—The organic matter contents of sediments deposited in Lakes Erie and Ontario contribute to the record of changes in the lake watersheds and aquatic ecosystems which have resulted from European settlement and cultural eutrophication of these systems over the past two centuries. Compositions of n-alkanes and n-alkanoic acids extracted from lake sediments track the clearing of the original natural forests and the appearance of agriculture in the watershed areas beginning about 1820. Aquatic productivity increased as runoff of soil nutrients increased. Cultural eutrophication in the 1950s is recorded in increases in organic C and in $n\text{-}C_{17}$ alkane concentrations. Diagenetic effects overprint source changes as shorter chain length and unsaturated lipid components are preferentially removed from the sedimentary record.

The geolipid fraction of sedimentary organic matter is a combination of the original, biologically synthesized lipid materials and diagenetically derived materials. Geolipid biomarker compounds and their distributions have proved useful in studies of the histories of organic matter accumulations in lake sediments. Differences in aquatic productivity are recorded in the types and amounts of geolipids incorporated into lake sediments and by their degree of diagenetic reworking (Cranwell 1978; Kawamura and Ishiwatari 1985). Straight-chain acids and alcohols, in particular, seem to be especially sensitive to preservational conditions (Meyers et al. 1984b; Wünsche et al. 1988; Ho and Meyers 1994) and hence signal changes in depositional environments. Hydrocarbon molecules are more resistant to such factors and thereby provide better indications of the original geolipid sources (e.g. Giger et al. 1980; Prahl and Carpenter 1984; Ho and Meyers 1994).

The combined distributions of sedimentary alkanes, fatty acids, alcohols, and sterols have enabled reconstructions of postglacial histories of organic matter deposition for Cam Loch, Scotland (Cranwell 1977), Heart Lake, New York (Meyers et al. 1984a), and Voua de la Motte, France (Wünsche et al. 1988). These lacustrine depositional histories include indications of changes in watershed vegetation, in rates of aquatic productivity, and in amounts of organic matter preservation in bottom sediments. Geolipid studies of sediment cores from Lake Huron, one of the Laurentian Great Lakes, have similarly revealed evidence of paleodepositional changes (Meyers et al. 1980; Meyers and Takeuchi 1981). Of particular prominence are the changes associated with conversion of the lake watershed from forested land to farm land and with more recent cultural eutrophication. Lake Huron is the second largest of the Laurentian Great Lakes and is generally considered to be impacted relatively less than other Great Lakes, except Lake Superior, by these human changes. We report here the recent geolipid depositional records of sediment cores from Lakes Ontario and Erie.

We obtained our sediment samples with a 40-cm box corer (50-cm square) at locations having different sedimentation rates so that accumulation of geolipids under different conditions could be studied. Stations E30 and G32 in the Rochester basin of Lake Ontario (Fig. 1) were sampled in 1981. Station LS in the eastern basin and station G16 in the central basin of Lake Erie (Fig. 1) were sampled in 1982.

The Lake Ontario cores are hand-collected subcores that were sectioned vertically by hydraulic extrusion into 1-cm intervals to 20 cm and 2-cm intervals from 20 to 40 cm on-board ship immediately after collection. The Lake Erie cores were similarly collected and sectioned. Sections were frozen on-board ship in solvent-cleaned glass jars, then freeze-dried within 3 months of collection. The data presented for each site come from a single box core.

Companion subcores from the box cores were dated by the ^{210}Pb methods used by Robbins and coworkers on Great Lakes cores (e.g. Robbins and Edgington 1975). The excess ^{210}Pb contents of the sediments were applied to a steady-state mixing model, and sediment accumulation rates were determined (Eisenreich et al. 1989; Schelske et al. 1988). Linear and mass accumulation rates of sediments determined by J. A. Robbins (pers. comm.) for the four locations are summarized in Table 1. Approximate deposition dates have been assigned to each section of the cores using the mass sedimentation rates determined on companion subcores and the cumulative dry weights of the present cores. Data are presented relative to deposition dates rather than core depths to facilitate discussion and comparisons among the sites.

Smearing of ^{137}Cs peaks in cores from both lakes is evidence of sediment mixing from bioturbation and indicates that the bottom waters have remained oxygenated, at least for most of each year. This mixing integrates the accumulation of a single year over a multiyear depth. The temporal resolution of near-surface sediments from station E30 is ~11 yr and that at station G32 is ~13 yr (Eisenreich et al. 1989). The resolution is finer where sedimentation rates are greater and where periods of sum-
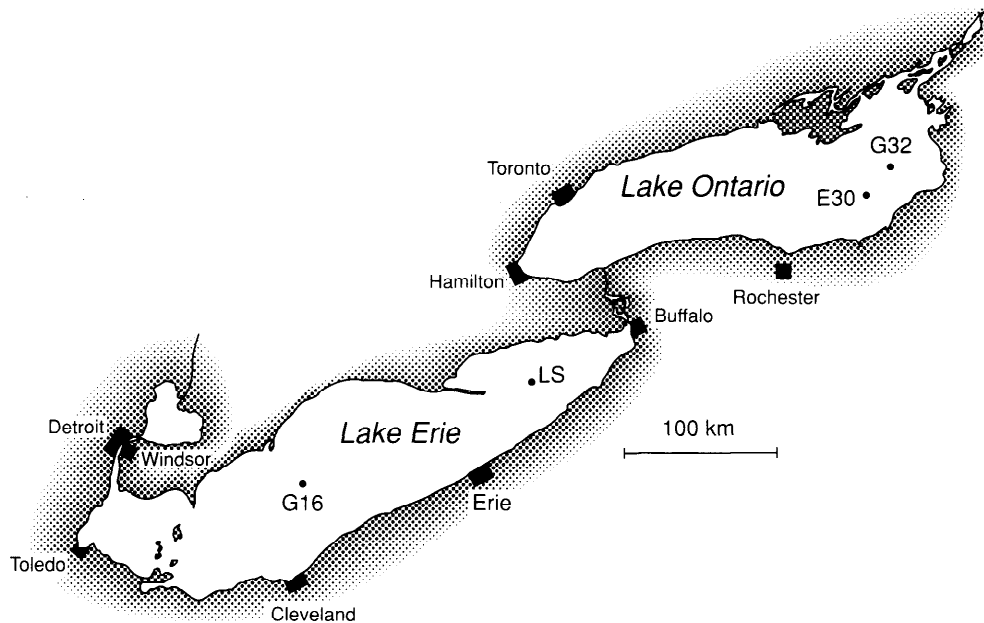
Fig. 1. Locations of box-coring stations in the central and eastern basins of Lake Erie and the Rochester basin of Lake Ontario. The respective water depths of stations G16 and LS in Lake Erie are 24 and 58 m and of stations E30 and G32 in Lake Ontario are 223 and 158 m. Sediment cores were dated by ^{210}Pb radiochronology (Eisenreich et al. 1989; Schelske et al. 1988).

mertime anoxia occur in bottom waters, such as at Lake Erie station G16 (Table 1).

Organic carbon concentrations (TOC) were determined by dry combustion of carbonate-free sediment samples at 1,000°C in a Leco IR-12 carbon analyzer. Carbonate was removed from intact dried sediment by treatment with concentrated sulfurous acid. Replicate analyses routinely agreed within a relative 3%.

Geolipids were Soxhlet extracted with a 1:1 mix of toluene and methanol, partitioned, saponified, and methylated (Leenheer et al. 1984). Saturated hydrocarbon and fatty acid methyl-ester fractions were isolated on alumina over silica chromatography columns and analyzed with a Carlo-Erba 4160 gas chromatograph equipped with on-column injection and a 30-m fused silica capillary column coated with SE30. Quantification was achieved with internal standards added before extraction and FID response factors determined from quantitative mixtures of known compounds. Data have been corrected for the small amounts of procedural contaminants determined by blank analyses.

The measured accumulation rates of sediments from the four locations differ substantially (Table 1) with the result that the ages of the basal sediments recovered by the 40-cm box corer are different. The approximate ages of the oldest sediments from the four stations are: E30, 1800; G32, 1870; G16, 1920; LS, 1940. Mass accumulation rates in Lake Ontario and Lake Erie have not been constant over the periods of depositional history recorded in the four cores. Schelske et al. (1988) determined that the rates increased by ~40% at station E30 and ~30%

at station G32 since the early part of this century. Part of this increase has been caused by increased accumulation of biogenic carbonate. A similar increase in modern sedimentation rates is likely in Lake Erie as well, but this inference has not been confirmed. These increases are postulated to result partially from enhancements of aquatic productivity since the mid-to-late 1800s (Schelske et al. 1983, 1988; Schelske and Hodell 1991, 1995) and partially from progressively more land erosion resulting from continued growth of human populations in the watersheds of the Great Lakes. These changes have also impacted accumulation of organic matter over these time periods.

Table 1. Sedimentation rates estimated from ^{210}Pb dating at four coring sites in Lakes Erie and Ontario. Cores were collected as part of the HI-SED Project (Great Lakes Environmental Research Laboratory).

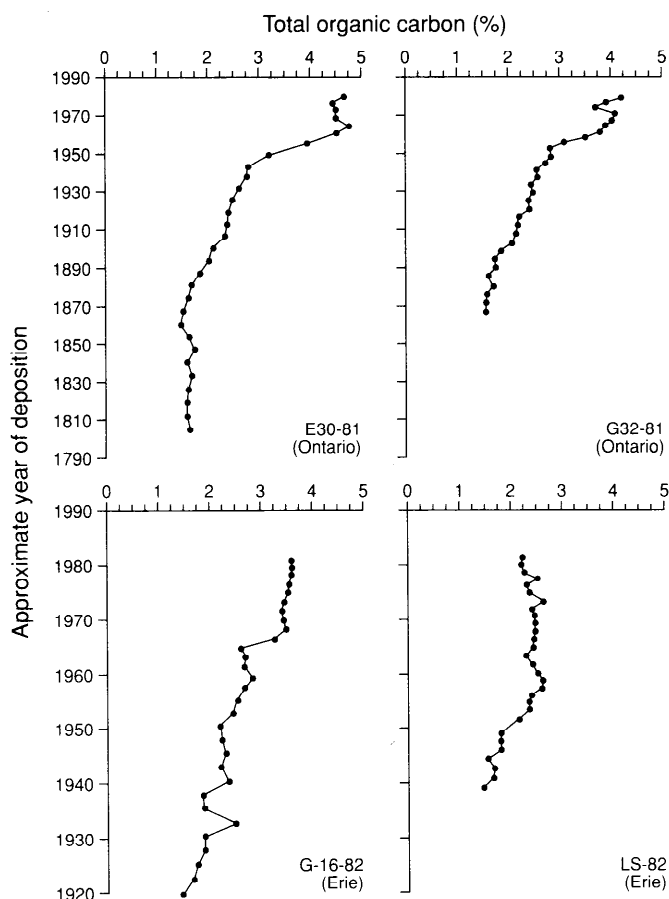|	Lake Ontario cores		Lake Erie cores	
	E30	G32	LS	G16
Water depth (m)	233	158	58	24
Sedimentation rate (cm yr^{-1})	0.26	0.39	0.86	0.91
Sediment mass accumulation rate (g m^{-2} yr^{-1})	440	770	2,820	1,360
Mixed depth (cm)	3–4	5–6	14–15	7–8
Temporal resolution (yr)	11.3	13.5	17.1	7.4

Total organic carbon (%)

Fig. 2. Total organic C (TOC) concentrations in sediments of the Lake Ontario and Lake Erie stations. Values of 1-cm intervals from the top 20 cm and of 2-cm intervals from 20- to 40-cm subbottom are plotted against year of deposition.

Total hydrocarbon concentration (mg g⁻¹ TOC)

Fig. 3. As Fig. 2, but of total extractable hydrocarbon contents relative to total organic C (TOC) concentrations.

TOC concentrations are elevated in the more recently deposited sediments and decrease with depth of burial (Fig. 2). The upper sediment intervals from the Lake Ontario stations have concentrations between 4 and 5%, whereas deeper sediments contain 1.5–2% organic C. Recent sediments from the Lake Erie stations have somewhat lower concentrations than those in Lake Ontario, but their deeper concentrations are similar, even though these intervals are not the same age.

The organic C sedimentary records in both lakes indicate important changes in organic matter deposition. The Ontario watershed was deforested between 1820 and 1850 (Schelske et al. 1983). The removal of forest cover resulted in increased delivery of dissolved P from land to the lake, enhancing aquatic productivity. Schelske et al. (1988) noted that organic C concentrations in these Lake Ontario cores follow the increases in phytoplankton abundance expected from the P enrichments. Organic C levels in sediments gradually increased in response to the higher productivity until about 1950. After this time, postwar growth of urban and suburban areas greatly enhanced nutrient delivery to the Great Lakes, causing a marked increase in both aquatic productivity and the rate of carbon accumulation.
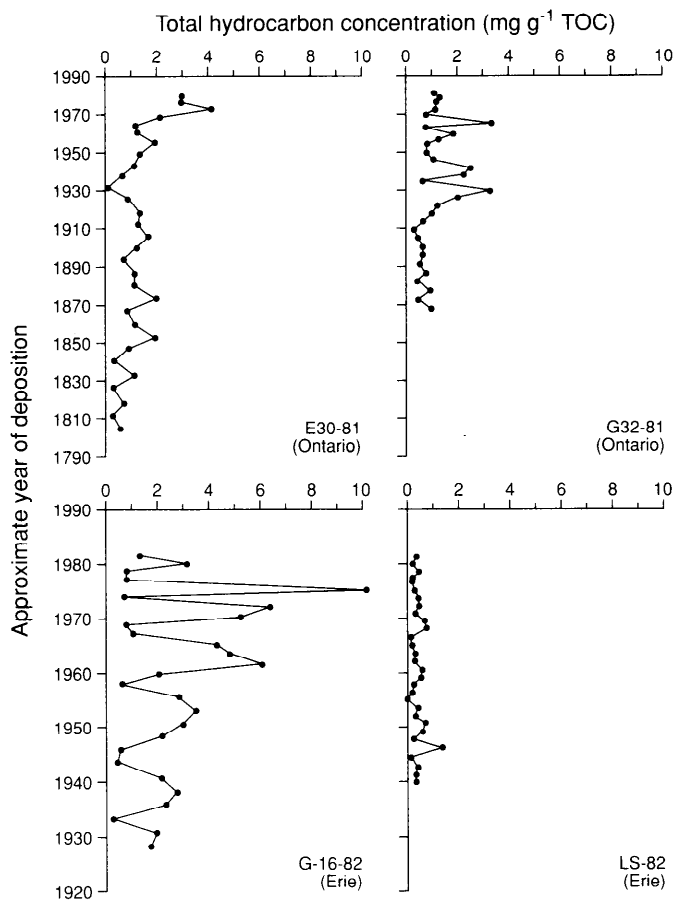
The Lake Erie records are not long enough to show the influence of deforestation, which occurred about 1880 in this watershed, but a consequence of postwar population increases is evident in the elevation of TOC concentrations starting ~1950 at both locations. Sediments deposited since 1965 at station G16 in Lake Erie exhibit an additional increase in organic C (Fig. 2). If sedimentary organic C concentration is a reliable proxy for aquatic productivity (e.g. Schelske et al. 1988; Schelske and Hodell 1995), this pattern indicates an additional increase in cultural eutrophication of Lake Erie starting in 1965.

Concentrations of extractable hydrocarbons, expressed as milligrams of total hydrocarbons per gram of TOC, are variable through the records of organic matter deposition provided by the sediment cores (Fig. 3). We present the concentrations relative to TOC to compensate for variations in total organic matter deposition and to identify periods when hydrocarbon accumulation was either enriched or depleted relative to total organic matter accumulation.

Of the four sedimentary hydrocarbon records, the nearly constant values in the data from station LS suggest that at this site there are no transient sources of hydrocarbons. Data from the other three sites show much more erratic records. The variability at these locations may originate from either numerous short-term variations in hydro-

carbon content of organic matter or fluctuations in the amounts of hydrocarbons preserved in the sedimentary record. Studies of relative apparent decomposition rates of organic matter settling in Lake Michigan show that hydrocarbons degrade two to three times slower than does total organic matter (Meyers and Eadie 1993). Because the record of TOC accumulation in these four cores is less variable than the hydrocarbon/organic C record, fluctuations in preservation cannot be an important cause of the variability seen in Fig. 3. Instead, these hydrocarbon accumulation records indicate that the proportions of hydrocarbons in the deposited organic matter have fluctuated in the source materials. Schelske and Hodell (1991) have noted a correspondence between C isotope contents, years of early onset of thermal stratification, and enhanced algal productivity in the sedimentary record at station G32. Fluctuations of this type in the supply of organic matter to the sediments, although integrated over the temporal resolutions of the core intervals, may impact the proportions of hydrocarbons in the records of Lakes Ontario and Erie.

A trend toward increasing proportions of hydrocarbons beginning ~1930 in core E30-81 (Fig. 3) may record progressively greater delivery of hydrocarbons from watershed sources. This site, the deepest in Lake Ontario, probably integrates the accumulation history of the entire Rochester basin because of sediment focusing. Similarly, core G16-82 from Lake Erie records pulses of increasingly larger proportions of hydrocarbons in organic matter deposited since 1930.

The relative contributions of the suite of different n-alkanes included in the total extractable hydrocarbon fractions provide information about the sources of these geolipids. For example, the presence of C_{27}, C_{29}, and C_{31} n-alkanes in sediment extracts shows that land-plant epicuticular waxes have been important sources of geolipids to the sediments (cf. Eglinton and Hamilton 1967; Cranwell 1973; Rieley et al. 1991). Algal contributions, in contrast, are indicated by the presence of n-C_{17} (cf. Blumer et al. 1971; Giger et al. 1980; Cranwell et al. 1987).

We used a ratio of these biomarker n-alkane source indicators to investigate possible changes in the terrigenous-aquatic mixture of hydrocarbons in these cores of Great Lakes sediment. The ratios of terrigenous to aquatic n-alkanes were estimated as

$$\text{terrigenous/aquatic ratio (TAR}_{HC})$$
$$= (C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19}).$$

Higher values for this parameter indicate increased watershed sources of lipid matter relative to aquatic sources.

The TAR_{HC} is generally >1 and quite variable in all the cores for sediments deposited since the beginning of the 1900s, but it is <1 and less variable in the older sedimentary record available from Lake Ontario (Fig. 4). Contributions of land-derived organic matter typically contain higher proportions of n-alkanes than do those from aquatic algae; consequently, parameters like the TAR_{HC} may overrepresent the absolute amounts from terrigenous sources (cf. Cranwell et al. 1987; Goossens et al. 1989; Meyers and Ishiwatari 1993). This ratio is none-
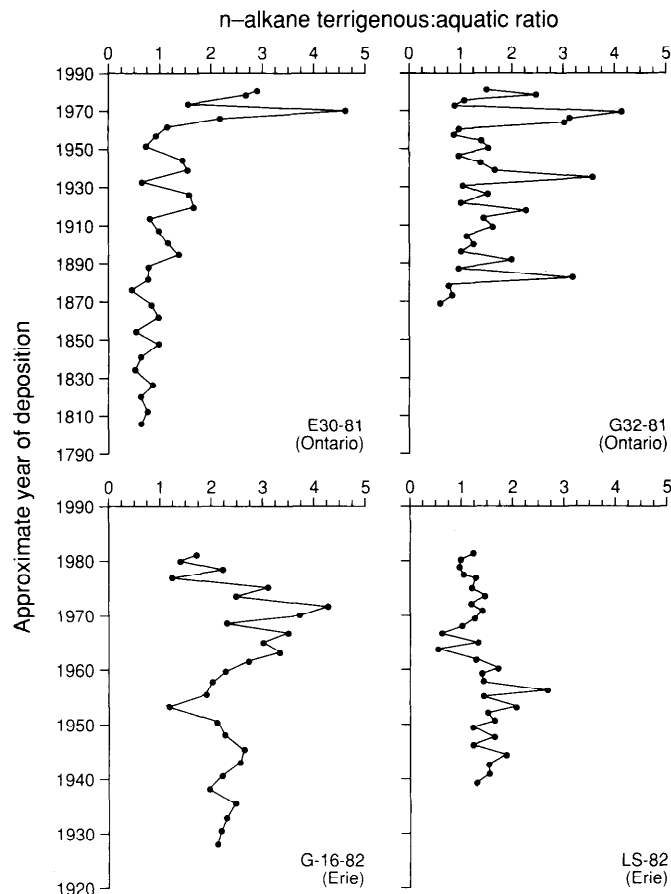

Fig. 4. As Fig. 2, but of ratios of terrigenous ($C_{27} + C_{29} + C_{31}$) to aquatic ($C_{15} + C_{17} + C_{19}$) n-alkanes.

theless valuable for determining changes in relative contributions of organic matter from land and lake flora. The contrast between the low TAR_{HC} values in older sediments and the higher and more variable values since the beginning of this century reflects a change in geolipid delivery to the lakes. The 20th century Lake Ontario sediments record progressively larger pulses of land-derived hydrocarbon delivery to this lake. This pattern reflects the increasingly urbanized character of the watershed, which has accelerated land runoff from paved roadways and from domestic wastewaters. Paradoxically, this factor has also increased nutrient supply to the lake flora and has caused eutrophication (e.g. Schelske et al. 1983; Schelske and Hodell 1991). The low TAR_{HC} values interspersed among the high 20th century values probably record periods of enhanced algal production inasmuch as organic C accumulation has increased continually since ~1870 (Fig. 2). The isotopic shift to more recent heavier $\delta^{13}C$ values (Schelske and Hodell 1991) shows that aquatic productivity in Lake Ontario has indeed increased over this period of sediment accumulation.

Modern chlorophyll and dissolved nutrient concentrations are equally elevated in the waters of Lakes Ontario and Erie, yet the concentrations of biogenic silica in sediments of the eastern basin of Lake Erie are an order of magnitude lower than in those of the Rochester basin of

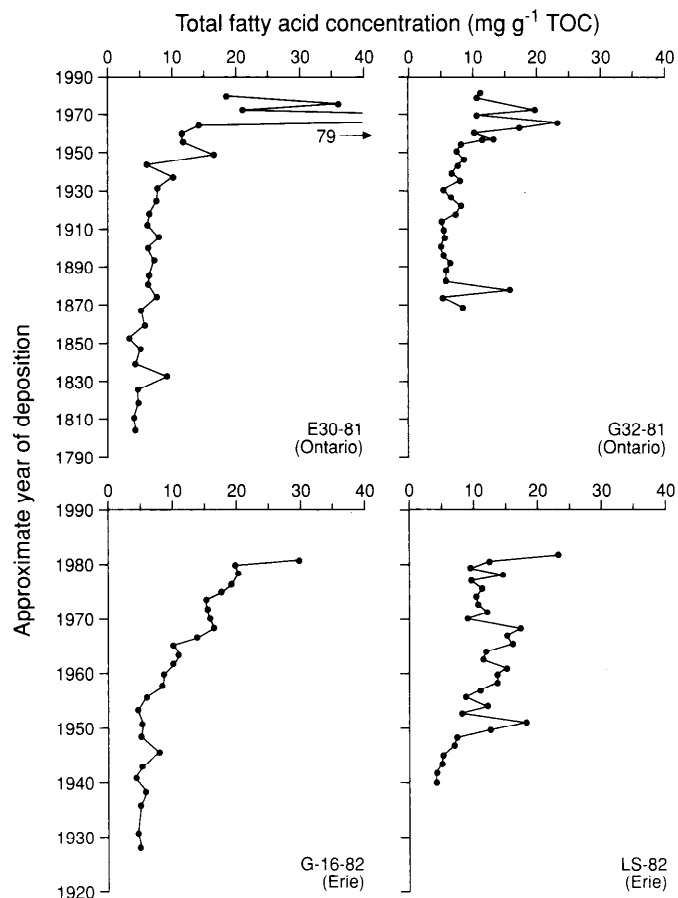

Fig. 5. As Fig. 2, but of total extractable fatty acid contents relative to TOC concentrations.

Lake Ontario (Schelske et al. 1983). Similarly, concentrations of organic C (Fig. 2) and contributions of total hydrocarbons to organic C (Fig. 3) are lower in sediments from station LS than in sediments of the same age from stations E30 and G32. The eastern basin of Lake Erie has a very high rate of sediment accumulation (Table 1)—over twice the rates in the Rochester basin. The high sedimentation rate simultaneously dilutes organic matter concentrations and enhances organic matter preservation. Hydrocarbons in general are less susceptible to microbial destruction during and after sedimentation than is most organic matter (e.g. Prahl and Carpenter 1984; Meyers and Eadie 1993), and the terrigenous long-chain hydrocarbons are less likely to be destroyed than are the short-chain algal hydrocarbons (Giger et al. 1980; Cranwell 1984). Where preservation of organic matter is enhanced, as in the recent sediments of station LS, the presence of larger amounts of normally degraded organic matter fractions diminishes the hydrocarbon proportions. At the same time, enhanced preservation of algal n-alkanes depresses TAR_{HC} values. The small decrease in TAR_{HC} values from ~ 1.5 in sediments deposited in 1940 to ~ 1 in 1980 sediments at station LS is most probably caused by eutrophication. The TAR_{HC} values of ~ 1 in pre-1880 sediments in Lake Ontario, however, reflect small contribu-

tions of terrigenous n-alkanes during the formerly oligotrophic conditions of the Great Lakes.

Concentrations of total extractable fatty acids are ~ 10 times greater than those of total hydrocarbons, relative to TOC, and they decrease with sediment depth at all four locations (Fig. 5). The proportion of total fatty acids in the organic C is generally between 5 and 10 mg fatty acids (g TOC)$^{-1}$ in sediments deposited prior to 1940. Increases in this proportion occur since this date at all four sites, and they correspond in time to increases in TOC concentrations (Fig. 2). The onset of the increases coincides in Lake Ontario with the productivity increase recorded by carbon isotope contents of sediments (Schelske and Hodell 1991; B. J. Eadie unpubl. data). As noted for the contributions of total hydrocarbons to the sediments at the four sites, fatty acids can originate from both lake and land sources. Variations in the relative contributions from algal productivity and from land runoff may be recorded in the fluctuations evident in Fig. 5.

Similarities between the fatty acid patterns for the four cores and the hydrocarbon patterns suggest that source changes, rather than degradation, have been the major factors controlling fatty acid concentration in the sediments. Fatty acids as a group are ~ 10 times more susceptible to degradation than are hydrocarbons (Haddad et al. 1992; Meyers and Eadie 1993). The concentration records of both the fatty acids and the hydrocarbons remain approximately in the same 10:1 ratio in all four cores. A steady fatty acid:hydrocarbon ratio would not be found if the downcore decreases in concentration were caused principally by postdepositional degradation. Instead, changes in source affecting total lipid contributions, including both acids and hydrocarbons, must be responsible.

As described for the hydrocarbon compositions of the sediment cores, we used a ratio of biomarker n-alkanoic acid source indicators to investigate possible changes in the terrigenous-aquatic mixture of fatty acids. Long-chain n-alkanoic acids, such as C_{24}, C_{26}, and C_{28}, are major components of the waxy coatings on land-plant leaves, flowers, and pollen (e.g. Rieley et al. 1991). Shorter chain C_{12}, C_{14}, and C_{16} n-acids are produced by all plants but are the dominant lipid components of algae (e.g. Cranwell et al. 1987). We used these source identifiers to calculate ratios of terrigenous to aquatic n-alkanoic acids as

$$\text{terrigenous/aquatic acid ratio (TAR}_{FA})$$
$$= (C_{24} + C_{26} + C_{28})/(C_{12} + C_{14} + C_{16}).$$

Higher values for this parameter may indicate increased watershed sources of lipid matter relative to aquatic sources, but they may also indicate preferential degradation of aquatic fatty acids relative to land-derived components.

The TAR_{FA} values from the two Lake Ontario stations are similar to each other but very different from those of the Lake Erie stations (Fig. 6). Like the TAR_{HC} profiles, the TAR_{FA} patterns are dominated by land-derived material, particularly in sediments deposited between 1960 and 1980. An increase in TAR_{FA} values starting ~ 1940 agrees with the pattern of progressive growth in the sub-

urban population of the Lake Ontario watershed, which has accelerated land runoff. The Lake Erie patterns, however, record an opposite trend—to diminished land-plant contributions and to enhanced algal productions. Furthermore, the Lake Ontario TAR_{FA} profiles record greater proportions of land-derived material than are indicated by the TAR_{HC} profiles (Fig. 4). These contrasts suggest that the fatty acid source records have been altered by diagenesis. It is probable that the Lake Ontario TAR_{FA} values exaggerate the magnitude of land-plant fatty acid contributions.

Selective degradation and other diagenetic effects commonly overprint fatty acid source signatures. Short-chain acids can be preferentially degraded by microbes during early diagenesis (e.g. Matsuda 1978; Haddad et al. 1992; Ho and Meyers 1994). Such degradation will elevate TAR_{FA} values, as possibly seen in the 1960–1980 portions of the Lake Ontario record. Postdepositional synthesis of fatty acids can also create changes in TAR_{FA} values. For example, microbial synthesis of secondary fatty acids from primary organic matter produces shorter chain components (e.g. Kawamura et al. 1987), which may depress TAR_{FA} values. This factor may contribute to the low TAR_{FA} values present at the sediment surface of all four stations (Fig. 6).

Organic matter in Lake Erie sediments appears to be diluted by high sediment accumulation rates and at the same time preserved better than in Lake Ontario sediments. As noted earlier, selective preservation impacts n-alkane compositions; it also affects n-alkanoic acid compositions. TAR_{FA} values in Lake Erie are significantly lower than in Lake Ontario. Much of this difference probably arises from better preservation of the typically more degradable shorter chain algal fatty acids, thereby lowering the TAR_{FA}. Nutrient availabilities in Lakes Erie and Ontario are virtually the same (Schelske et al. 1983), and algal productivities should therefore be similar. The difference between the modern fatty acid source records must result from differences in preservation rates.

Concentrations and compositions of fatty acid in general are less variable than those of the hydrocarbon contents of the sediments at the four locations. Interaction of the competing processes of selective preservation and microbial resynthesis evidently diminishes the actual fluctuations in geolipid source character, which are better preserved in the TAR_{HC} values.

Further evidence of postdepositional changes that occur to fatty acids in these sediments is provided by the ratio of the unsaturated n-C_{16} acid over its saturated analog. Unsaturated acids are especially susceptible to early diagenetic degradation in lake sediments (e.g. Matsuda and Koyama 1977). The ratios for both locations in Lake Erie are about twice those of the Lake Ontario cores (Fig. 7). Sedimentation rates in Lake Erie at these sites are higher than at the Lake Ontario sites (Table 1). Faster burial in the sediments of Lake Erie evidently improves the preservation of the normally poorly preserved unsaturated n-C_{16} acid. The variability present in the Lake Ontario sediments may represent fluctuations in sediment remixing, which impacts preservation of reactive organic matter.
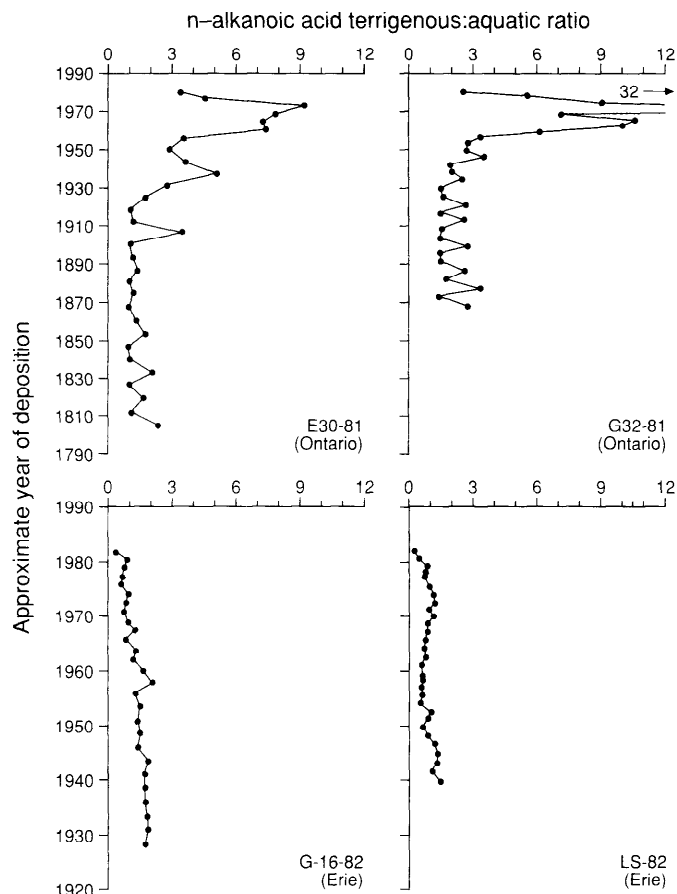

Fig. 6. As Fig. 2, but of ratios of terrigenous (C_{24} + C_{26} + C_{28}) to aquatic (C_{12} + C_{14} + C_{16}) n-alkanoic acids. Lower terrigenous: aquatic ratios in Lake Erie reflect higher sedimentation rates, which retard diagenetic degradation of aquatic fatty acid components.

The unsaturated/saturated fatty acid profiles for the two cores from each lake are quite similar to each other (Fig. 7). This uniformity suggests that the process of diagenesis overprints source contributions with respect to the more reactive components of organic matter and that organic matter diagenesis rates are consistent within a given set of depositional conditions.

Our comparison of the geolipid contents of sediments from dated cores from Lakes Ontario and Erie shows that different aspects of these components can be used to obtain information about the histories of production and preservation of sedimentary organic matter in lakes. Sediment organic C concentrations and hydrocarbon compositions record changes in the major influences on organic matter accumulation in lake basins, including deforestation and urbanization, and reveal the effects of postdepositional processes such as bioturbation. Ratios of terrigenous to aquatic n-alkane and n-alkanoic acid components reflect differences in the urban-rural character of these two basins and the history of urbanization and population pressure in both basins. Concentrations of total hydrocarbon relative to organic C suggest changes in geolipid sources that overprint the total organic matter
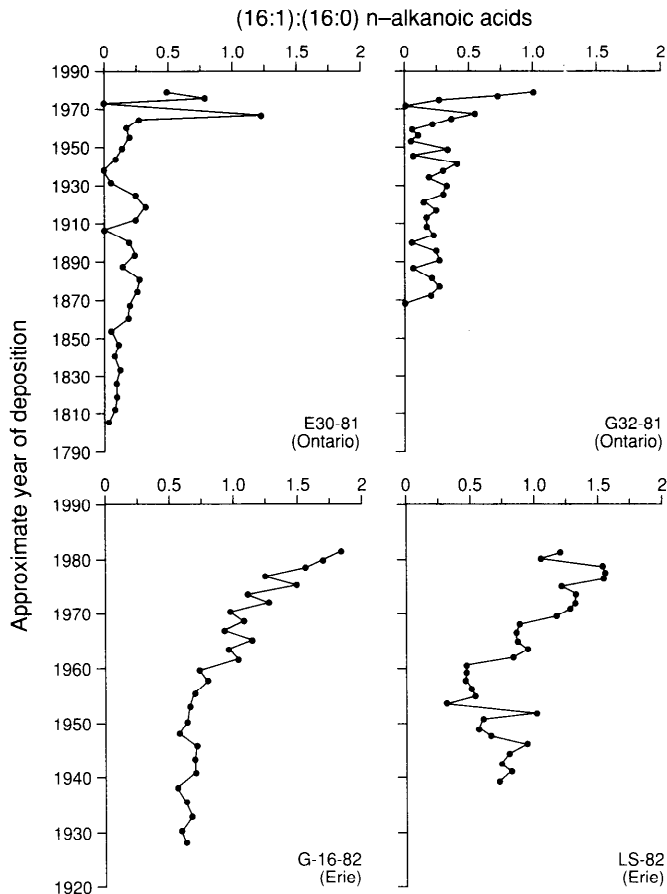
Fig. 7. As Fig. 2, but of ratios of monounsaturated to saturated *n*-C$_{16}$ fatty acids. Higher sedimentation rates in Lake Erie retard diagenetic degradation of unsaturated acids.

depositional record. Diagenetic effects influence the total extractable fatty acid concentrations, which therefore do not record source changes as well as do the total extractable hydrocarbon concentrations.

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Ecosystem-specific patterns in the relationship between zooplankton and POM or microplankton $\delta^{13}C$

Abstract—Measurements of plankton $\delta^{13}C$ from 28 temperate lakes show that zooplankton are depleted in ^{13}C relative to smaller planktonic size fractions. A broad literature survey indicates that this is a general pattern in lakes but not in marine and estuarine plankton communities, where zooplankton are generally enriched in ^{13}C relative to particulate organic matter (POM) or microplankton. Marine plankton thus conform to the assumptions that pelagic food webs are essentially driven by phytoplankton and that POM or small planktonic size classes largely reflect algal carbon, which is transferred to zooplankton with a slight enrichment in ^{13}C. The plankton of lakes and possibly of estuaries, however, do not conform to this expectation. We show that there is a continuum in the $\delta^{13}C$ differences between POM and zooplankton from open ocean to coastal areas and estuaries and that a similar pattern occurs from unproductive to highly productive lakes. These differences probably reflect both the degree in POM dilution by nonalgal sources of organic carbon and depth-related changes in the isotopic signature of phytoplankton in lakes and suggest systematic differences in organic carbon flow pathways among aquatic ecosystems.

Carbon stable isotope ratios are commonly used in ecological studies to trace the flow of organic matter through both aquatic and terrestrial food webs (Fry and Sherr 1984; Peterson and Fry 1987). Robust and clearly defined source end-points are a requisite in the use of stable isotope analysis for discriminating and tracing carbon pathways in ecological systems. In the study of pelagic food webs in particular, one of these end-points is almost invariably phytoplankton (e.g. Fry and Sherr 1984). Phytoplankton, however, are difficult to isolate from other living and nonliving suspended materials, so that total particulate organic matter (POM) or plankton collected in small (<30 μm) pore-size screens (microplankton) are routinely used as surrogate end-points, with the implicit assumption that most of this material is algal in composition. Because organisms under controlled laboratory conditions are slightly enriched in ^{13}C relative to their diets (Fry et al. 1984; DeNiro and Epstein 1978), larger zooplankton are likewise expected to be slightly enriched in ^{13}C relative to POM or the microplankton on which